

## Claims:

1. A method for calculating a ring-down time from a ring-down signal derived from a cavity ring-down spectroscopy instrument, wherein the ring-down time is responsive to conditions within an optical resonator of the instrument, the method comprising:
  - a) selecting a low pass filter having a bandwidth equal to  $X/T_{\text{short}}$ , where  $T_{\text{short}}$  is a shortest expected ring-down time and  $X$  is a predetermined constant in a range from about 2 to about 10;
  - b) passing the ring-down signal through the filter to provide a filtered signal  $f(t)$ , where  $t$  is time;
  - c) constructing a digital ring-down signal comprising data points  $(t_i, f(t_i))$  having values  $f(t_i)$ , wherein  $t_i$  denotes a set of points substantially uniformly spaced in time which fall within a selected fitting window; and
  - d) calculating the ring-down time using a curve fitting method applied to the digital ring-down signal.
2. The method of claim 1, wherein said low pass filter is an analog filter.
3. The method of claim 1, wherein said low pass filter is a digital filter.
4. The method of claim 1, where  $X$  is about 3.
5. The method of claim 1, further comprising calculating an estimate  $T_1$  of the ring-down time by averaging the time separation of data points of said filtered signal which differ in value by a predetermined ratio.
6. The method of claim 5, wherein said predetermined ratio is substantially equal to  $e^{(1/2)}$ .
7. The method of claim 5, wherein a duration of said fitting window is in a range from about  $5T_1$  to about  $15T_1$ .

8. The method of claim 7, where said duration is about  $10T_1$ .
9. The method of claim 1, further comprising the step of searching said filtered signal for a trigger data point having a value which is a local maximum and which exceeds a predetermined upper threshold.
10. The method of claim 9, further comprising the step of calculating an estimate  $T_1$  of the ring-down time by averaging the time separation of data points of said digital ring-down signal which differ in value by a predetermined ratio.
11. The method of claim 10, wherein a time interval between said trigger data point and a first data point of said digital ring-down signal is in a range from about  $0.2T_1$  to about  $0.5T_1$ .
12. The method of claim 11, where said time interval is about  $0.35T_1$ .
13. The method of claim 9, wherein an earliest point of said digital ring-down signal is selected to be the first point of said filtered signal following said trigger data point whose value is less than  $Y$  times the value of said trigger data point, where  $Y$  is a predetermined constant in a range from about 0.65 to about 0.85.
14. The method of claim 13, where  $Y$  is about 0.74.
15. The method of claim 5, wherein said curve fitting method comprises:
  - f) calculating a first estimate  $B_1$  of a background level by averaging the values of data points in a background range of said digital ring-down signal;
  - g) constructing a binned signal by subdividing said digital ring-down signal into a predetermined number  $N_{bin}$  of adjacent sections, each having a duration  $T_{bin}$ , and averaging the values of data points within each of the sections;

- h) calculating a corrected binned signal having values which are substantially equal to the values of said binned signal minus  $B_1$ ;
- i) calculating an estimate  $A_2$  of an amplitude and an improved estimate  $T_2$  of the ring-down time using weighted linear regression of a logarithm of the values of said corrected binned signal;
- j) calculating a second estimate  $B_2$  of the background level which is substantially equal to the average of the values of the data points of said digital ring-down signal within a background determination window minus the average of an exponential with amplitude  $A_2$  and time constant  $T_2$  within the background determination window;
- k) calculating a corrected digital signal having values which are substantially equal to the values of said digital ring-down signal minus  $B_2$  within a final fitting window; and
- l) calculating said ring-down time using weighted linear regression of a logarithm of the values of said corrected digital signal.

16. The method of claim 15, wherein said background range is from about  $8T_1$  to about  $10T_1$ .

17. The method of claim 15, wherein said duration  $T_{bin}$  is substantially equal to  $0.5T_1$ .

18. The method of claim 15, wherein said predetermined number  $N_{bin}$  is about 10.

19. The method of claim 15, wherein said background determination window is from about  $5T_1$  to about  $10T_1$ .

20. The method of claim 15, wherein said final fitting window is from about 0 to about  $4T_2$ .

21. The method of claim 15, wherein the weighted linear regression of step i is weighted according to the values of said corrected binned signal.

22. The method of claim 15, wherein the weighted linear regression of step l is weighted according to the values of said corrected digital signal.

23. The method of claim 5, wherein said curve fitting method comprises:

f) calculating an estimate B1 of a background level by averaging the values of data points in a background range of said digital ring-down signal;

g) calculating a corrected digital signal having values which are substantially equal to the values of said digital ring-down signal minus B1 within a final fitting window;

h) calculating an estimate  $\tau^*$  of the ring-down time using weighted linear regression of a logarithm of the values of said corrected digital signal;

i) calculating an estimated error  $\Delta B$  in the estimate B1 of the background using the estimate  $\tau^*$ ;

j) calculating an estimated error  $\Delta \tau$  in the estimate  $\tau^*$  using the estimated error  $\Delta B$  and the estimate  $\tau^*$ ; and

k) calculating said ring-down time using the estimate  $\tau^*$  and the estimated error  $\Delta \tau$ .

24. The method of claim 23, wherein said background range is from about  $8T1$  to about  $10T1$ .

25. The method of claim 23, wherein said final fitting window is from about 0 to about  $4T2$ .

26. The method of claim 23, wherein the earliest point in said fitting window is at  $t = 0$ , and wherein said background window extends from  $t = t_a$  to  $t = t_b$ , and wherein  $\Delta B$  is calculated according to  $\Delta B = \tau^* (\exp(-t_a/\tau^*) - \exp(-t_b/\tau^*)) / (t_b - t_a)$ .

27. The method of claim 23, wherein the step of calculating the ring-down time comprises setting the ring-down time substantially equal to  $\tau^* / (1 + \Delta \tau)$ .

28. The method of claim 23, wherein the weighted linear regression of step h is weighted according to the values of said corrected digital signal.

29. A method for calculating a ring-down time from a ring-down signal derived from a cavity ring-down spectroscopy instrument, wherein the ring-down time is responsive to conditions within an optical resonator of the instrument, the method comprising:

- a) generating a ring-down table having a multiplicity of data points, each point having a time and a value, by substantially uniformly time sampling said ring-down signal;
- b) calculating an estimate  $T1$  of the ring-down time by averaging the time separation of data points within said table which differ in value by a predetermined ratio;
- c) constructing a digital ring-down signal comprising consecutive data points in said table which fall within a selected fitting window;
- d) calculating a first estimate  $B1$  of a background level by averaging the values of data points in a background range of said digital ring-down signal;
- e) constructing a binned signal by subdividing said digital ring-down signal into a predetermined number  $N_{bin}$  of adjacent sections, each having a duration  $T_{bin}$ , and averaging the values of data points within each of the sections;
- f) calculating a corrected binned signal having values which are substantially equal to the values of said binned signal minus  $B1$ ;
- g) calculating an estimate  $A2$  of an amplitude and an improved estimate  $T2$  of the ring-down time using weighted linear regression of a logarithm of the values of said corrected binned signal;
- h) calculating a second estimate  $B2$  of the background level which is substantially equal to the average of the values of the data points of said digital ring-down signal within a background determination window minus the average of an exponential with amplitude  $A2$  and time constant  $T2$  within the background determination window;
- i) calculating a corrected digital signal having values which are substantially equal to the values of said digital ring-down signal minus  $B2$  within a final fitting window; and
- j) calculating said ring-down time using weighted linear regression of a logarithm of the values of said corrected digital signal.

30. The method of claim 29, wherein a duration of said fitting window is in a range from about  $5T1$  to about  $15T1$ .

31. The method of claim 30, where said duration is about  $10T_1$ .
32. The method of claim 29, wherein said background range is from about  $8T_1$  to about  $10T_1$ .
33. The method of claim 29, wherein said duration  $T_{bin}$  is substantially equal to  $0.5T_1$ .
34. The method of claim 29, wherein said predetermined number  $N_{bin}$  is about 10.
35. The method of claim 29, wherein said background determination window is from about  $5T_1$  to about  $10T_1$ .
36. The method of claim 29, wherein said final fitting window is from about 0 to about  $4T_2$ .
37. The method of claim 29, wherein the weighted linear regression of step g is weighted according to the values of said corrected binned signal.
38. The method of claim 29, wherein the weighted linear regression of step j is weighted according to the values of said corrected digital signal.
39. A method for calculating a ring-down time from a ring-down signal derived from a cavity ring-down spectroscopy instrument, wherein the ring-down time is responsive to conditions within an optical resonator of the instrument, the method comprising:
- a) generating a ring-down table having a multiplicity of data points, each point having a time and a value, by substantially uniformly time sampling said analog ring-down signal;
  - b) calculating an estimate  $T_1$  of the ring-down time by averaging the time separation of data points within said table which differ in value by a predetermined ratio;
  - c) constructing a digital ring-down signal comprising consecutive data points in said table which fall within a selected fitting window;

- d) calculating an estimate B1 of a background level by averaging the values of data points in a background range of said digital ring-down signal;
- e) calculating a corrected digital signal having values which are substantially equal to the values of said digital ring-down signal minus B1 within a final fitting window;
- f) calculating an estimate  $\tau^*$  of the ring-down time using weighted linear regression of a logarithm of the values of said corrected digital signal;
- g) calculating an estimated error  $\Delta B$  in the estimate B1 of the background using the estimate  $\tau^*$ ;
- h) calculating an estimated error  $\Delta\tau$  in the estimate  $\tau^*$  using the estimated error  $\Delta B$  and the estimate  $\tau^*$ ; and
- i) calculating said ring-down time using the estimate  $\tau^*$  and the estimated error  $\Delta\tau$ .

40. The method of claim 39, wherein a duration of said fitting window is in a range from about  $5T_1$  to about  $15T_1$ .

41. The method of claim 40, where said duration is about  $10T_1$ .

42. The method of claim 39, wherein said background range is from about  $8T_1$  to about  $10T_1$ .

43. The method of claim 39, wherein said final fitting window is from about 0 to about  $4T_2$ .

44. The method of claim 39, wherein the earliest point in said fitting window is at  $t = 0$ , and wherein said background window extends from  $t = t_a$  to  $t = t_b$ , and wherein  $\Delta B$  is calculated according to  $\Delta B = \tau^* (\exp(-t_a/\tau^*) - \exp(-t_b/\tau^*)) / (t_b - t_a)$ .

45. The method of claim 39, wherein the step of calculating the ring-down time comprises setting the ring-down time substantially equal to  $\tau^* / (1 + \Delta\tau)$ .

46. The method of claim 39, wherein the weighted linear regression of step f is weighted according to the values of said corrected digital signal.

47. A cavity ring-down instrument comprising:

- a) an optical source;
- b) a ring-down cavity in optical communication with the source;
- c) a detector positioned to receive radiation emitted from the ring-down cavity, the detector providing a ring-down signal;
- d) a filter which receives the ring-down signal and provides a filtered signal  $f(t)$  where  $t$  is time, wherein the filter has a bandwidth substantially equal to  $X/T_{\text{short}}$ , where  $T_{\text{short}}$  is a shortest expected ring-down time and  $X$  is a predetermined constant substantially in a range from about 2 to about 10; and
- e) a processor, wherein the processor constructs a digital ring-down signal comprising data points  $(t_i, f(t_i))$  having values  $f(t_i)$ , wherein  $t_i$  denotes a set of points substantially uniformly spaced in time which fall within a selected fitting window, and wherein the processor calculates a ring-down time using a curve fitting method applied to the digital ring-down signal.

48. A cavity ring-down instrument comprising:

- a) an optical source;
- b) a ring-down cavity in optical communication with the source;
- c) a detector positioned to receive radiation emitted from the ring-down cavity, the detector providing an analog ring-down signal; and
- d) a processor, wherein the processor substantially uniformly samples the analog ring-down signal to generate a ring-down table having a multiplicity of data points, each point having a time and a value, and wherein the processor constructs a digital ring-down signal comprising consecutive data points in the ring-down table which lie within a selected fitting window, and wherein the processor calculates an estimate  $T1$  of a ring-down time by averaging the time separation of data points within said fitting window which differ in value by a predetermined ratio, and wherein the processor calculates a first estimate  $B1$  of a background level by averaging the values of data points in a



background range of said digital ring-down signal, and wherein the processor constructs a binned signal by subdividing said digital ring-down signal into a predetermined number  $N_{\text{bin}}$  of adjacent sections, each having a duration  $T_{\text{bin}}$ , and averaging the values of data points within each of the sections, and wherein the processor calculates a corrected binned signal having values which are substantially equal to the values of said binned signal minus B1, and wherein the processor calculates an estimate A2 of an amplitude and an improved estimate T2 of the ring-down time using weighted linear regression of a logarithm of the values of said corrected binned signal, and wherein the processor calculates a second estimate B2 of the background level which is substantially equal to the average of the values of the data points of said digital ring-down signal within a background determination window minus the average of an exponential with amplitude A2 and time constant T2 within the background determination window, and wherein the processor calculates a corrected digital signal having values which are substantially equal to the values of said digital ring-down signal minus B2 within a final fitting window, and wherein the processor calculates said ring-down time using weighted linear regression of a logarithm of the values of said corrected digital signal.

49. A cavity ring-down instrument comprising:

- a) an optical source;
- b) a ring-down cavity in optical communication with the source;
- c) a detector positioned to receive radiation emitted from the ring-down cavity, the detector providing an analog ring-down signal; and
- d) a processor, wherein the processor substantially uniformly samples the analog ring-down signal to generate a ring-down table having a multiplicity of data points, each point having a time and a value, and wherein the processor constructs a digital ring-down signal comprising consecutive data points in the ring-down table which lie within a selected fitting window, and wherein the processor calculates an estimate T1 of a ring-down time by averaging the time separation of data points within said fitting window which differ in value by a predetermined ratio, and wherein the processor calculates a first estimate B1 of a background level by averaging the values of data points in a background range of said digital ring-down signal, and wherein the processor calculates a

corrected digital signal having values which are substantially equal to the values of said digital ring-down signal minus B1 within a final fitting window, and wherein the processor calculates an estimate  $\tau^*$  of the ring-down time using weighted linear regression of a logarithm of the values of said corrected digital signal, and wherein the processor calculates an estimated error  $\Delta B$  in the estimate B1 of the background using the estimate  $\tau^*$ , and wherein the processor calculates an estimated error  $\Delta\tau$  in the estimate  $\tau^*$  using the estimated error  $\Delta B$  and the estimate  $\tau^*$ , and wherein the processor calculates the ring-down time using the estimate  $\tau^*$  and the estimated error  $\Delta\tau$ .